

# Record critical current density in bulk MgB<sub>2</sub> using carbon-coated amorphous boron with optimum sintering conditions

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**Abstract.** We report on the synthesis and characterization of a sintered bulk MgB<sub>2</sub> material produced at an *optimized sintering temperature* with a *varying content of carbon-encapsulated amorphous boron*. A series of MgB<sub>2</sub> bulks was prepared with 0%, 1.5%, 2.8%, 7.3%, 12% and 16.5% of carbon-encapsulated boron. In the samples with 12% of carbon-encapsulated boron, Mg and MgB<sub>2</sub>C<sub>2</sub> formation was observed.  $T_c$  was around 38.4 K for the pure MgB<sub>2</sub> and decreased with increasing carbon content up to 25 K for 16.5 % of carbon-encapsulated boron. The highest  $J_c$  values of 470 kA/cm<sup>2</sup> and 310 kA/cm<sup>2</sup>, in the self-field and 1 T, respectively, were achieved at 20 K, in the MgB<sub>2</sub> sample with 1.5% of carbon-encapsulated boron. It proved that the optimized sintering conditions together with the appropriate amount of the carbon-coated boron were able to bring critical current performance of bulk MgB<sub>2</sub> material up to the level necessary for real technical applications.

## 1. Introduction

A significant effort has been made in the development of MgB<sub>2</sub> materials processing, characterization, and applications [1, 4]. The superconducting transition temperature of MgB<sub>2</sub> is significantly lower than that of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> “Y-123”, however, MgB<sub>2</sub> benefits from some BCS-like superconducting features, e.g. a large coherence length and weak magnetic relaxation. It allows for a better Josephson junction fabrication. Within the group of intermetallic superconductors, the critical temperature is still rather high, which with use of a refrigerator allows for a rather low cooling costs. The cheaper technology and the quite high critical current density ( $J_c$ ) in the polycrystalline state make this material promising for applications in power industry, magnetic resonance imaging (MRI), fault current limiters (FCL), Josephson junctions and SQUIDS, energy storage, levitation devices and powerful super-magnets operating at around 20 K [4, 5].

For superconducting super-magnet applications, it is necessary to produce a good quality and high performance bulk MgB<sub>2</sub> material with high  $J_c$  and low production cost. To improve the critical current density of the MgB<sub>2</sub> material, a variety of processing techniques have been developed including chemical doping [6], refining of the initial particle size by ball milling [7], and irradiation [8]. As a result, the transport  $J_c$  values at liquid helium temperature and 10 T reached the level of 10<sup>5</sup> A/cm<sup>2</sup> for Si-doped MgB<sub>2</sub> samples. Similar improvements were also observed with additions of carbon, boron carbide, carbon nanotubes, carbohydrates or hydrocarbons, graphene oxide, Ni-Co-B nanoparticles [9,10]. However, the critical current density values of MgB<sub>2</sub> materials still need a further improvement for high



magnetic field applications. Recent microstructural observations by AFM and SEM indicated that a proper sintering time is very important to control the grain size of the  $\text{MgB}_2$  material [11]. X-ray diffraction, DC magnetization and scanning electron microscopy (SEM) analyses proved that single-phase and homogenous  $\text{MgB}_2$  bulks were produced by sintering at 775 °C and 800 °C, which exhibited the highest critical current density recorded so far. The samples sintered at 775 °C for 1 h showed  $J_c$  of 270 kA/cm<sup>2</sup> at 20 K [12]. A trapped field value of 1.51 T at 20 K was achieved in such  $\text{MgB}_2$  samples of 20 mm diameter and 7 mm thickness. The simple sintering route is attractive for mass production of bulk  $\text{MgB}_2$  materials. However, a further improvement in  $J_c$  is needed for such a simple technology. Utilizing the carbon-encapsulated boron might help, since carbon doping of  $\text{MgB}_2$  superconducting wires had very positive results, record critical current densities being reported in such tapes and wires [13]. Recent reports on bulk  $\text{MgB}_2$  samples doped by carbon encapsulated boron showed superior critical current density as compared to pure samples [14,15]. Processing optimization is still needed for bulk  $\text{MgB}_2$  material to reach a uniform carbon dispersion in the bulk  $\text{MgB}_2$  material. One of the points is to find an optimum content of the carbon-encapsulated boron in the compound.

In the present paper, we report on superconducting properties, X-ray diffraction, and chemical analysis of the carbon-coated boron bulk  $\text{MgB}_2$  materials fabricated by a simple sintering method, exhibiting a high  $J_c$  and a homogenous carbon distribution in the whole sample.

## 2. Experimental details

The bulk  $\text{MgB}_2$  samples were fabricated by using in-situ solid state reaction. The commercial powders (Furu-uchi Chemical Corporation, Japan) of Mg metal (99.9% purity, 200 meshes) and amorphous B powder (99% purity, 300 meshes) were mixed in the nominal ratio of Mg: B = 1: 2. To test the effect of carbon-coated boron on flux pinning and the associated  $J_c$  value, five kinds of carbon-encapsulated B powder (98% purity) were utilized in production of the bulk  $\text{MgB}_2$  material, namely PVZ-C15 (1.5% C), PVZ-C28 (2.8% C), PVZ-C73 (7.3% C), PVZ-C120 (12% C) and PVZ-C165 (16.5% C). All the carbon-encapsulated B powders were produced at PAVEZYUM, Advanced Chemicals, Turkey. More details of the carbon-encapsulated B powder production can be found elsewhere [14]. The starting powders were thoroughly ground in a glove box in argon atmosphere. The powder mixture was pressed into pellets of 20 mm in diameter and 7 mm thick using a uniaxial press of 200 MPa. The consolidated pellets were then wrapped in tantalum foils and subjected to the heat treatment in Ar atmosphere in a tube furnace. All samples were heated to the target sintering temperature of 805 °C and kept there for 3 h in flowing argon gas. Finally, the temperature was lowered to room temperature at a cooling rate of 100 °C/h. The constituent phases of the samples were identified with a high-resolution automated X-ray powder diffractometer (RINT2200), using Cu-K $\alpha$  radiation generated at 40 kV and 40 mA. The microstructure of these samples was studied with a scanning electron microscope (SEM) and chemical composition was estimated by SEM by EDX analysis.

Small specimens with dimensions of 1.5×1.5×0.5 mm<sup>3</sup> were cut from bulk  $\text{MgB}_2$  samples and subjected to the measurements of critical temperature ( $T_c$ ) and magnetization hysteresis loops ( $M$ - $H$  loops) in applied magnetic fields from -1 to +5 T at 20 K using a SQUID magnetometer (Quantum Design, model MPMS5). The magnetic  $J_c$  values (in MA/cm<sup>2</sup>) were estimated based on the extended Bean critical state model using the relation

$$J_c = 20 \Delta m / [a^2 d (b-a/3)] \quad (1)$$

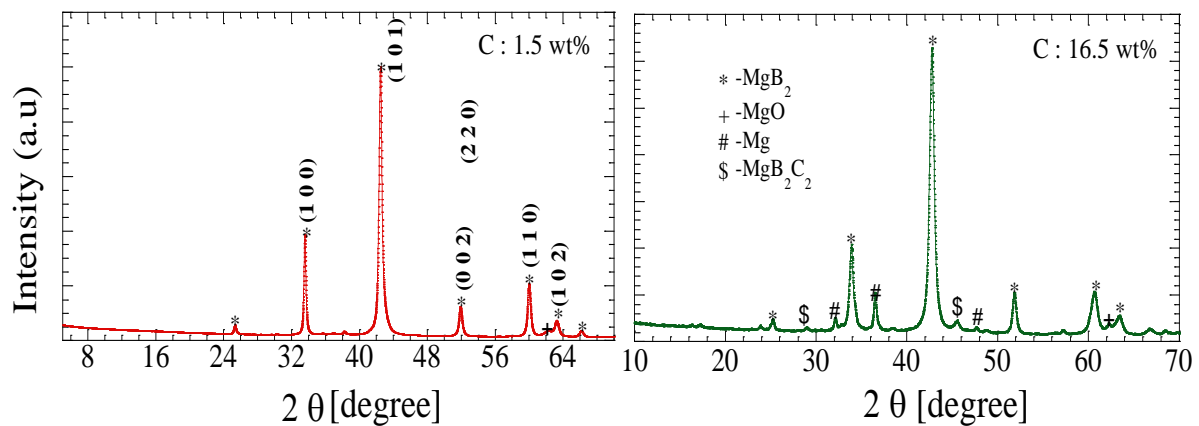
where  $d$  is the sample thickness,  $a$ ,  $b$  are cross sectional dimensions,  $b \geq a$ , ( $a$ ,  $b$ ,  $d$  in mm) and  $\Delta m$  (in emu units, 1 emu=10<sup>-3</sup> Am<sup>2</sup>) is the difference of magnetic moments during increasing and decreasing field in the  $M$ - $H$  loop [16].

## 3. Results and discussion

X-ray diffraction patterns of bulk  $\text{MgB}_2$  materials produced using various carbon-encapsulated boron powders showed that lower contents of C always gave a single-phase bulk  $\text{MgB}_2$  material. Fig.1 shows

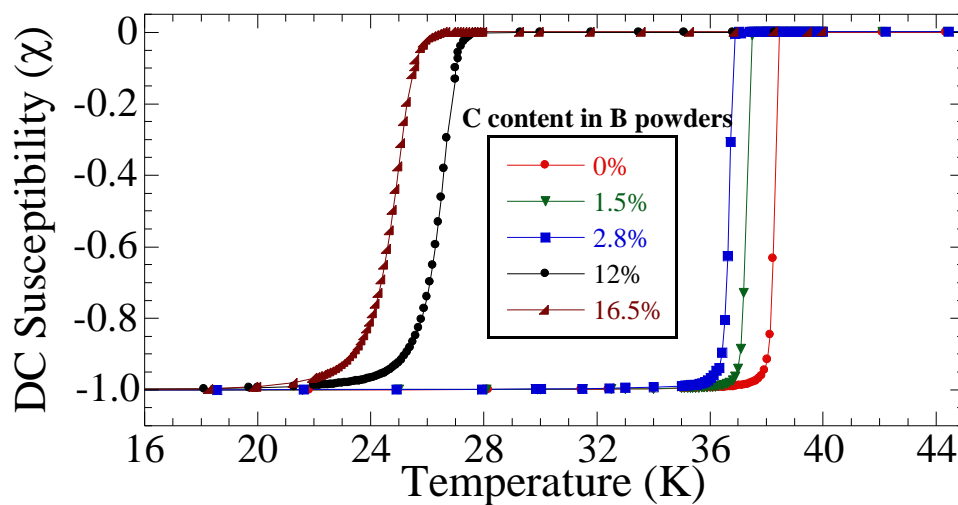
the X-ray diffraction patterns of bulk  $\text{MgB}_2$  materials produced utilizing a low and a high content of C in the boron powder. Both samples were sintered at 805 °C in argon atmosphere. From the figure it follows that the main phase was  $\text{MgB}_2$  in both samples, similar with our earlier report [3].

However, with the C content in the B powders around 12 wt% and 16.5wt% the minor impurity phases i.e.  $\text{MgB}_2\text{C}_2$  and Mg phases appeared (see Fig. 1, right). Several other authors also found the minor phase of  $\text{MgB}_2\text{C}_2$  in bulk  $\text{MgB}_2$  samples with carbon-doping [9, 17]. In our case, we did not observe any minor phase in the samples with a lower carbon content in the carbon-encapsulated boron powder than 7.5%. Thus, less content of carbon than 7.5% in the carbon-encapsulated boron is needed to produce a  $\text{MgB}_2$  material without impurity phases.

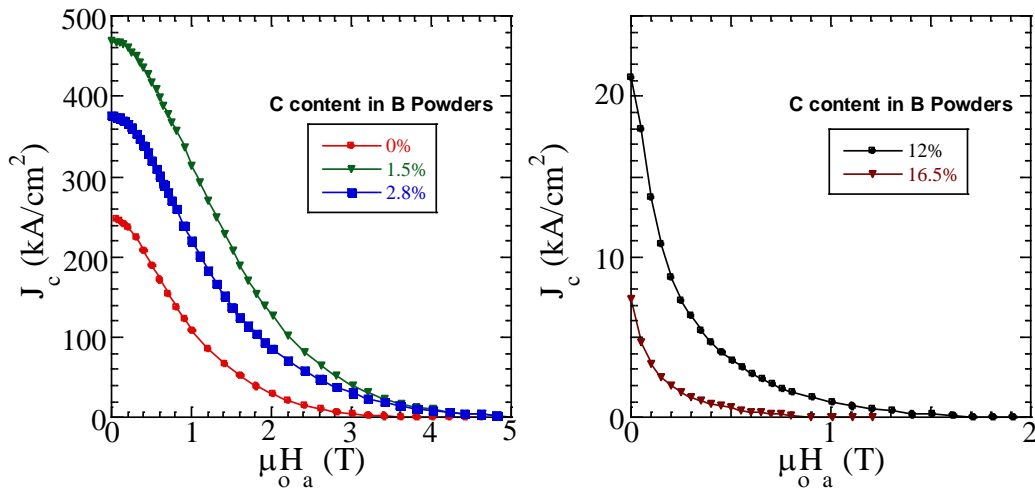


**Figure 1.** X-ray diffraction patterns of bulk  $\text{MgB}_2$  superconductor produced using the carbon-encapsulated boron powders and sintered at 805 °C in argon atmosphere. Low C content in B powders (left figure); high C content in B powders (right figure).

Figure 2 shows the DC magnetic susceptibility in magnetic field of 1 mT as a function of temperature for the  $\text{MgB}_2$  materials produced various contents of carbon in the carbon-encapsulated boron. All samples exhibited a sharp superconducting transition. A high onset  $T_c$  close to 38.5 K was found for the pure  $\text{MgB}_2$  sample, with increasing carbon content in the carbon encapsulated boron  $T_c$  decreased.

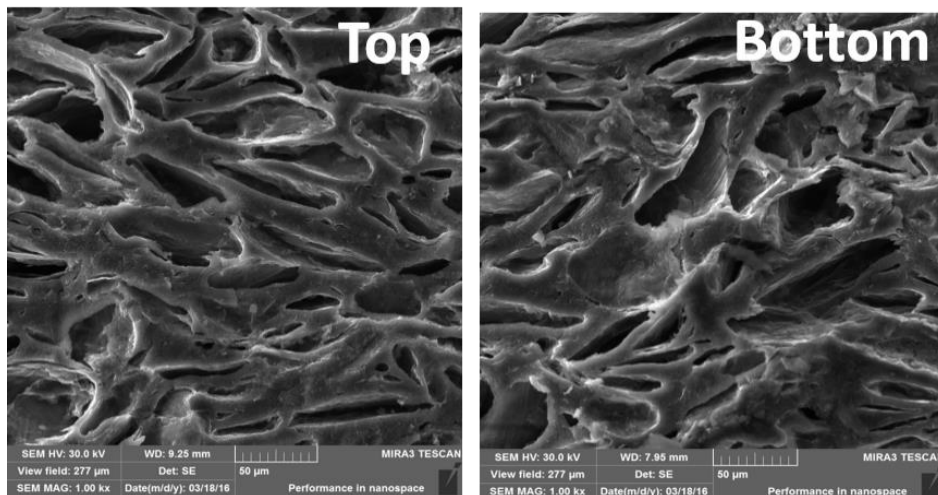


**Figure 2.** Superconducting transition in the bulk  $\text{MgB}_2$  materials produced with various carbon contents in the carbon-encapsulated B powders, all sintered at 805 °C for 3h in argon.



**Figure 3.** Field dependence of the critical current densities ( $T=20\text{K}$ ) for  $\text{MgB}_2$  superconductor produced using the carbon-encapsulated boron powders and sintered at  $805^\circ\text{C}$  in argon atmosphere. Lower C content in B powders (left figure); Higher C content in B powders (right figure).

The samples with low C contents, 1.5wt% and 2.8 wt%, showed  $T_c$  (onset) 37.6 K and 37 K, only slightly lower than for the pure sample [18]. On the other hand, the samples with high carbon contents in carbon-encapsulated boron showed rather lower superconducting transitions, close to 25 K (see Fig. 2). In  $\text{MgB}_2$  tapes and wires doped by carbon it is believed that C substitutes for boron, which stiffens the optical  $E_{g2}$  phonon mode, strongly linked to the anisotropic  $\sigma$  band and hence to a lower transition temperature [9]. The results indicate that the carbon-encapsulated boron powders with a low content of C (<2.8%) will help to optimize production of high quality bulk  $\text{MgB}_2$  materials.



**Figure 4.** Low magnification scanning electron micrographs of the  $\text{MgB}_2$  superconductor produced with the carbon-encapsulated boron powder with 2.8 wt% content of carbon and sintered at  $805^\circ\text{C}$  in argon atmosphere.

The critical current density at 20 K as a function of applied magnetic field is shown in Figure 3. for bulk  $\text{MgB}_2$  materials with various contents of carbon in the carbon-encapsulated boron powder, all sintered at  $805^\circ\text{C}$  for 3h in argon atmosphere. High  $J_c$  values were achieved in bulk  $\text{MgB}_2$  material produced with low contents of carbon in the carbon-encapsulated boron (Fig.3, left). In the sample with 1.5% of

carbon in the carbon-encapsulated boron the self-field critical current density of 470 kA/cm<sup>2</sup> was observed. The high-field  $J_c$  and the irreversibility field,  $H_{irr}$ , values increased in the samples with the carbon content in the carbon-encapsulated boron up to 2.8wt% and decreased in samples with a higher carbon contents. Especially the samples with 12wt% and 16.5% of carbon showed a dramatic decrement in the high-field  $J_c$  and  $H_{irr}$  values (see Fig.3, right). It is consistent with the shift of the experimental temperature to the rather low  $T_c$  in these materials.

To elucidate microstructure, SEM by EDX analysis was performed the MgB<sub>2</sub> sample with 2.8 wt% of carbon in the carbon-encapsulated boron powder. The SEM image taken at a lower magnification shows that the MgB<sub>2</sub> matrix contains numerous voids of various shapes and sizes (Fig. 4). The porosity presents a serious problem in the sintered bulk MgB<sub>2</sub> material. The microstructure and chemical analysis were tested at several positions of the same pellet, on its top and bottom as presented in Fig. 4 and Table 2. The carbon content was measured by EDAX without calibration, therefore the measured values are only semi-quantitative. In any case, the obtained carbon contents in various positions are quite uniform (Table 1). These results prove that the carbon content over the MgB<sub>2</sub> pellet is quite homogenous, which indicates that the carbon-encapsulated boron with a low optimum amount of carbon is an effective way how to produce a high quality MgB<sub>2</sub> with effective pinning structure and electromagnetic performance at a reasonably high operating temperature.

**Table 1.** Carbon content estimated by SEM-EDAX analysis for MgB<sub>2</sub> superconductor produced using the 2.8 wt% carbon-encapsulated boron powder.

Position	1	2	3	4	average
Bottom	3.2	3.0	2.6		2.86
Top	3.0	3.0	2.8	2.8	2.90

#### 4. Conclusions

High performance bulk MgB<sub>2</sub> materials were prepared utilizing the boron powders pre-encapsulated by carbon in various contents and sintered at optimum sintering conditions. The magnetization results confirmed that 1.5wt% of carbon in the carbon-encapsulated boron powder did not affect much the superconducting transition temperature, in contrast to the MgB<sub>2</sub> materials using the carbon-encapsulated boron powders with 12wt% or 16.5% carbon. The MgB<sub>2</sub> material produced utilizing the 1.5 wt% carbon-encapsulated boron powder and sintered at 805 °C for 3 h showed a high critical current density of 470 kA/cm<sup>2</sup> and 310 kA/cm<sup>2</sup> at 20 K in self-field and 1 T, respectively. This indicates that the carbon-encapsulated boron powder has a high potential for use in batch production of large single grain MgB<sub>2</sub> bulks, reducing the production time and cost, just this being the key to transfer the technology from laboratory to industrial production.

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